

METHOD OF FORMING SILICON CARBIDE FILMSField of the Invention

The present invention relates to nitrogen doped silicon carbide layers referred to herein as SiCN and, more particularly to a method of forming low dielectric constant, low leakage current and high compressive stress nitrogen doped silicon carbide layers.

Background of the Invention

Integrated circuits have evolved into complex devices that include multiple levels of metal layers to electrically interconnect discrete layers of semiconductor devices on a single semiconductor chip. Recently, with the evolution of higher integration and higher density of integrated circuit components, the demand for greater speed of the data transfer rate is required. For this reason, an insulating film having high compressive stress, low leakage current, low dielectric constant to give the small RC delay is employed.

As the device dimensions continuously shrink, the RC time delay of the interconnect system becomes one of the most important limitation factors to the integrated circuits performance. The RC delay is directly proportional to the resistivity of the metal and the dielectric constant of the dielectric. In order to minimize the signal propagation delay, it is inevitable to use low dielectric constant materials as the inter-layer and intra-layer dielectrics (ILD). While many low-k ($k < 3.0$) materials have been used as ILDs, silicon nitride with a high dielectric constant ($k > 7.0$) is still the primary candidate for the Etch Stop Layer (ESL) required in copper damascene structures. Thus, it is desirable to replace silicon nitride by new materials with lower dielectric constants to further reduce the effective dielectric constant of the Cu interconnect system. In recent years, increasing interest has been focused on the study of high stress and thermally stable low-k silicon carbide based films deposited by PECVD using organosilicon gases.

Furthermore, to reduce the size of interconnection lines and vias is to change the wiring materials from the conventional aluminum (Al) to copper (Cu) wiring having low electric resistance.

However, to produce a semiconductor device having multi-layered copper wiring, a low dielectric constant insulating layer is formed as the interlayer insulating film on the copper wiring.

The use of copper as the interconnect material has various problems. For example, copper is easily diffused into the low dielectric constant insulating film from the copper wiring, thus increasing the leakage current between the upper and lower wiring.

The use of silicon carbide films as copper diffusion barrier layers has been published in United States Patent 5,800,878. The dielectric constant of this film is about 5, and in addition it is used as copper diffusion barrier layers for 130nm-nodes Large Scale Integration (LSI) technologies where the dielectric constant of the interlayer dielectric film is 3.

For next generation, 100nm/65nm-nodes Ultra Large Scale Integration (ULSI) technologies, the reduction of interconnect capacitance is important for suppressing the signal delay as well as the power consumption. Interlayer dielectric films with dielectric constant less than 2.5 are used with copper damascene structures. To decrease the effective dielectric of fine pitched lines, further reduction in the dielectric constant is necessary not only for the inter layer dielectric film itself but also the supporting dielectric films such as hard mask, etch stop layers and copper diffusion barrier layers.

The interface between copper and copper diffusion barrier layer is known to be the key point for the electro-migration reliability of copper interconnects. The interface between copper and the copper diffusion barrier layer is the dominant diffusion path. However, there is no report on the identification of the dominant path for copper interconnects. On the other hand, the interface can be not only the dominant path but also the electro-migration induced void nucleation site.

The strength of adhesion between copper and diffusion layer would affect the electro-migration induced void nucleation because electro-migration induced void nucleates when copper atom at the interface is stripped away from the diffusion layer. Films with high compressive stress provide better adhesion with copper. It is also suggested that in order to prevent the migration of metal atoms, the film has to have high compressive stress such as above 200MPa where the stress is stable even after being directly exposed to air at room temperature of about 20 to 30 °C. Furthermore, the leakage current and dielectric constant of

such film at 1MV/cm has to be less than that of 1×10^{-8} A/cm² and less than 5.0 respectively. SiCN films with dielectric constant less than 5 such that the leakage current at 1MV/cm is less than 1×10^{-8} A/cm² are suggested to be suitable to substitute for such films.

Using the silicon carbide film as an etch stop film was developed and presented in USP5800878. A dielectric constant of the silicon carbide film is approximately 5. Silicon carbide films are applied to LSI devices using copper wiring in combination with carbon-containing silicon oxide films, whose dielectric constant is approximately 3. There are several different types of compositions for what is generally called silicon carbide films. One type is a silicon carbide film comprising Si, C and H. This film's stress and dielectric constant change if it is left in the atmosphere. This is due to the oxidation of the top surface of the silicon carbide film. The method to minimize the oxidation of carbon containing materials, such as silicon carbide, with an inert gas plasma such as helium (He), Argon (Ar) is published in JP laid-open patent 2001/0060584. This inert gas plasma treatment only minimizes the top surface of the silicon carbide film from getting oxidized, however, no changes/improvements to the film properties are observed.

The method of forming nitrogen doped silicon carbide (SiCN), oxygen doped silicon carbides (SiCO) has been published in United States Patent Application Publication 2001/0030369, United States Patent Application Publication 2002/0027286, United States Patent Application Publication 2001/0051445, and United States Patent Application Publication 2001/0031563. Furthermore; these films have been proposed as copper diffusion barrier layers. Though a silicon carbonitride layer has been proposed as a copper diffusion barrier layer with low leakage current, its dielectric constant is high and film stress is less compressive such as 5.5 and 100MPa respectively.

In case of oxygen doped silicon carbide, although its dielectric constant is relatively low, such as less than 5, it cannot sufficiently refrain from increasing the leakage current. To decrease the leakage current to a sufficient level, the oxygen must be introduced much more into the silicon carbide film.

However, to do so, the leakage current can be reduced up to a satisfactory level, nevertheless a new problem is caused such that the surface of the copper wiring is oxidized and thus the barrier insulating film and the inter dielectric layer is ready to peel.

Summary of the Invention

Thus, it is desired to develop a new method of forming etch stop layers and copper diffusion barrier layers that can be employed in the next generation, 100nm/65nm-nodes Ultra Large Scale Integration (ULSI) technologies, where the copper damascene structures are used.

The main characteristics of etch stop layers and copper diffusion barrier layers such as nitrogen doped silicon carbide films (SiCN) developed using various embodiments of the present invention are as follows:

- a) The dielectric constant is less than 5.0
- b) The film stress is compressive and is above 200MPa.
- c) No changes to its film properties such as changes to the film stress or changes to film dielectric constant are observed even when directly exposed to air at a room temperature between 20 °C to 30 °C.
- d) The leakage current at 1MV/cm is extremely low, such as less than 1×10^{-8} A/cm².
- e) The etch selectivity of SiCN to SiOC (as intermediate dielectric), is higher than 3.

According to one preferred embodiment of the present invention, a method of forming low dielectric constant, low leakage current with high compressive stress silicon carbide film for use in integrated circuit fabrication processes is provided. The silicon carbide film is deposited on a substrate by introducing alkyl silicon compounds such as divinyl-dimethylsilane ($\text{Si}(\text{CH}=\text{CH}_2)_2(\text{CH}_3)_2$), tri-methylsilane ($\text{SiH}(\text{CH}_3)_3$) or tetra-methylsilane ($\text{Si}(\text{CH}_3)_4$) referred to herein as TMS, a substantial source of nitrogen such as ammonia (NH_3) and nitrogen(N_2) and an inert gas such as argon (Ar), helium (He), krypton (Kr), neon (Ne) or xenon (Xe) in the presence of an electric field in a plasma CVD reactor.

A mixture of high and low frequency RF power, such that high frequency RF power is in the range of 13.56MHz to 30MHz and low frequency RF power is in the range of 200kHz to 500kHz, wherein the ratio of low frequency to total power is less than about 0.5, generates the electric field. The leakage current and dielectric constant of the silicon carbide in this invention is decreased by introducing excess amount of nitrogen and inert gas.

Brief Description of the Drawings

FIGURE 1 is a schematic cross-sectional view of an exemplary plasma chemical vapor deposition device.

FIGURES 2a – 2i illustrate a dual damascene structure in which a silicon carbide layer can be used.

FIGURE 3 illustrates an exemplary sequence (deposition recipe) for forming a SiCN film.

Detailed Description of the Preferred Embodiment

Disclosed herein is a method for depositing a silicon carbide film having a low dielectric constant with low leakage current and high compressive stress onto a substrate in a CVD chamber, comprising the steps of providing a silicon source, carbon source, nitrogen source and an inert gas in a reaction zone containing a substrate, and reacting the silicon and carbon and nitrogen source in the presence of a plasma to deposit a low dielectric constant and low leakage current silicon carbide film on the substrate.

A mixture of high and low frequency RF power generates the electric field, wherein the ratio of low frequency to total power is less than about 0.5. The leakage current and dielectric constant in the resulting silicon carbide film is directly related to the carbon concentration, amount of nitrogen and inert gas introduced.

Silicon Carbide Layer Formation

In one preferred embodiment of the present invention, a silicon carbide layer is formed by reacting a gas mixture including, silicon source, carbon source, nitrogen source and an inert gas into a plasma enhanced chemical vapor deposition (PECVD) chamber. Details of the processing system are illustrated in Fig. 1.

Fig. 1 is a schematic cross section of an exemplary plasma CVD device according to a preferred embodiment. A plasma CVD device 1, which is used to form a thin film on a semiconductor wafer 9 or other substrate, comprises a reaction chamber 2, a support 3 provided within the reaction chamber to support the semiconductor wafer 9, a shower-head 4

that is positioned to face the support 3 and is used to spray reaction gas uniformly onto the semiconductor wafer 9, an outlet 20 to exhaust reaction gases and byproducts from the reaction chamber 2, and a remote plasma discharge chamber 17. Cleaning gas for the remote plasma chamber 17 is supplied through a conduit 18 having an inlet port 16 leading to a main flow controller 14 and a valve 15. The remote plasma discharge chamber 17 is linked to the showerhead 4 via piping 6 and valve 7. The remote plasma discharge chamber 17 generates active species using radio-frequency oscillating output energy of the designated frequency, and the piping 6 is made of materials that are not corroded by the active species.

The support 3 that is provided within the reaction chamber 2 and that is used to support the semiconductor wafer 9 is made of anodized aluminum alloy and is grounded 27 to constitute one side of an electrode of plasma discharge. The reaction chamber 2 of the illustrated embodiment is thus a plasma CVD chamber configured for in situ (in chamber) plasma generation. The support 3 includes a heater 5 having a ring-shape heating element 24 embedded therein. The semiconductor wafer's temperature is controlled at a predetermined temperature using a temperature controller (not shown). The support 3 is connected to a driving mechanism 26 that moves the support 3 up and down through a support piston 25.

Within the reaction chamber 2, the showerhead 4 is provided at a position facing the support 3. In the showerhead 4, thousands of fine holes are provided to inject reaction gas onto the semiconductor wafer 9. The showerhead is electrically connected to a radio-frequency oscillator 8 and 8' via matching circuit 10 and constitutes another electrode for plasma discharge. To bring reaction gas to be used for film formation from the showerhead 4, a reaction gas conduit 12 is connected to a mass flow controller 14 with a shut-off valve 15 near the outlet from the flow controller and a valve 11 controlling flow to the piping 6. The number of the gas conduits is not limited to one. According to the type of reaction gas, any number of gas conduits can be installed. One end of the gas conduit 12 constitutes a gas inlet port 13 to cause reaction gas to flow in and the other end constitutes a reaction gas exit port to cause gas to flow to the inlet 29 of the showerhead 4.

The outlet 20 is connected to a vacuum exhaust pump (not shown) through piping 19. Between the outlet 20 and the vacuum pump, a conductance-controlling valve 21 is provided to regulate pressure within the reaction chamber 2. The conductance-controlling valve 21 is

electrically connected to an external regulator 22 and a pressure gauge 23, preferably provided to measure pressure within the reaction chamber 2. The wafer 9 is inserted into the chamber 2 through a port 28 controlled by a gate valve 30.

The silicon and carbon source may be an alkyl silicon compound having a general formula $Si_xC_yH_z$, where x has a range from 1 to 2, y has a range from 1 to 6, and z has a range from 6 to 20. For example, divinyl-dimethylsilane, tri-methylsilane, and tetra-methylsilane among others maybe used as the alkyl silicon compound. Nitrogen source is ammonia (NH3) and nitrogen (N2). Helium (He), argon (Ar), neon (Ne), krypton (Kr) and xenon (Xe) maybe used for the inert gas.

In general, the deposition process parameters of forming a silicon carbide film on a 200mm silicon wafer include a substrate temperature range of about 200°C to about 400°C (more preferably 330-380°C), a chamber pressure of about 300Pa to 1000Pa, an alkyl silicon compound flow rate of about 100sccm to 1000sccm, nitrogen source flow rate such as ammonia (NH3) and nitrogen (N2) of about 100sccm to 500sccm and 100sccm to 1000sccm respectively, and an inert gas flow rate of about 200sccm to 5000sccm. This creates a ratio of the inert gas flow rate to alkyl silicon compound is in the range of about 1:1 to about 1:10. The process also includes a mixed frequency RF power having at least a first RF power with a frequency in a range of about 13MHz to 30MHz (high frequency) with a power in a range of about 100 Watts to 2000 Watts; and at least a second RF power with a frequency in a range of about 100kHz to 500kHz (low frequency) with a power in the range of about 50 Watts to 500 Watts. Thus the ratio of low frequency to total power is less than about 0.5, and the RF power source generates the electric field. Preferably the first RF power is in the range of 300 to 1000W and the second RF power is in the range of 50 to 250W. The second RF power with a frequency in a range of 300kHz to 450kHz is preferably used in combination with the first RF power.

The ratio of the second RF power to the total mixed frequency power is preferably less than about 0.5 to 1.0. The above process parameters provide a deposition rate for the silicon carbide layer in the range of about 100nm/min to 350nm/min, when implemented on a 200mm substrate in a deposition chamber.

SiCN film formation

As an exemplary process for growing SiCN film on a substrate according to the present invention the parameters listed in TABLES 1 through 3 were used:

TABLE 1

Parameter	Range
Tetra-methylsilane (TMS) flow rate	10sccm ~ 1000sccm
Ammonia (NH ₃) flow rate	10sccm ~ 1000sccm
Nitrogen (N ₂) flow rate	10sccm ~ 3000sccm
Helium (He) flow rate	50sccm ~ 10000sccm
Pressure	100Pa ~ 2000 Pa
Low RF Power	50W ~ 5000W
High RF Power	20W ~ 1000W
Substrate Temperature	200°C ~ 450°C

TABLE 2

Parameter	Preferred Range
Tetra-methylsilane (TMS) flow rate	100sccm ~ 500sccm
Ammonia (NH ₃) flow rate	50sccm ~ 500sccm
Nitrogen (N ₂) flow rate	50sccm ~ 2000sccm
Helium (He) flow rate	100sccm ~ 5000sccm
Pressure	200Pa ~ 1500 Pa
Low RF Power	100W ~ 2000W
High RF Power	50W ~ 500W
Substrate Temperature	250°C ~ 400°C

TABLE 3

Parameter	More Preferred Range
Tetra-methylsilane (TMS) flow rate	200sccm ~ 300sccm
Ammonia (NH3) flow rate	100sccm ~ 300sccm
Nitrogen (N2) flow rate	100sccm ~ 1000sccm
Helium (He) flow rate	500sccm ~ 3000sccm
Pressure	300Pa ~ 1000 Pa
Low RF Power	200W ~ 1000W
High RF Power	50W ~ 200W
Substrate Temperature	300°C ~ 380°C

Film Forming Conditions/Sequence

To deposit SiCN layer on 200mm wafer, a reactive gas source such as tetra-methylsilane (TMS) and a substantial source of nitrogen such as ammonia (NH3) and nitrogen (N2) is introduced into the reaction zone. Helium can be used as an inert gas.

Figure 3 discloses an example of the present invention. After a semiconductor substrate is carried into a reaction chamber and is heated at a given temperature, in the step 46 'Bringing in He', helium 48, which is an inert gas, is brought into the reaction chamber at a determined flow within the limits of 100sccm to 3000sccm, controlling the pressure inside the reaction chamber 49 at a determined value within the limits of 300Pa to 1000Pa. In step 47 'Bringing in TMS, N2 and NH3', TMS 50 is brought into the reaction chamber at a determined flow within the limits of 200sccm to 300sccm, N2 51 is brought into the reaction chamber at a determined flow within the limits of 100sccm to 1000sccm and NH3 52 is brought into the reaction chamber at a determined flow within the limits of 100sccm to 300sccm. For bringing in He, N2, NH3 and TMS gas, a ramp-up method in which a flow of respective gases is increased from zero to a given value at a specific rate during predetermined time frames is adopted. This method is used to prevent floating of particles in the reaction chamber and adhering of the particles to the semiconductor substrate. Such a

phenomenon is caused by a rise in a pressure in the reaction chamber resulted from the drastic gas flow into the reaction chamber.

Once the gas flow such as TMS, NH₃, N₂ and He is stabilized as shown in step 53, RF power with a frequency of 27.12MHz is applied in the range of 200 to 1000W and RF power with a frequency 400kHz is applied in the range of 50 to 500W. In this step silicon carbide film is formed.

The basic film properties of the SiCN film deposited above are shown in TABLE 5. Furthermore, no major changes either to dielectric constant or to stress of this film were observed even when exposed to air at room temperature of 20°C to 30°C.

Furthermore, when annealing is performed at 400°C under nitrogen atmosphere for 10 hours, a change in the film stress is observed but still it remains compressive. The change in the stress is less than about 100MPa. It is presumed that the SiCN film deposited according to the embodiments described above has a good thermal stress behavior. As mentioned earlier in the introduction films with high compressive stress provides better adhesion with copper. It can also be presumed that due to not changing the stress from compressive to tensile, good adhesion behavior between barrier insulating film and inter dielectric layer is expected. Leakage current and dielectric constant of silicon carbide film at 1MV/cm is less than that of 1×10^{-8} A/cm² and less than 5.0 respectively which consequently suggests that the silicon carbide films according to this embodiment is suitable to use as copper diffusion barrier layer as well as etch stopper.

The silicon carbide films deposited by the PECVD process described herein have significantly lower concentration of hydrogen which result in lower dielectric constant, lower leakage current and high compressive stress in comparison to the conventional silicon carbide films. The silicon carbide films can be deposited without a mixture of low and high frequency. However, the preferred mixture of high and low radio frequency corrects adverse film properties caused by the bombardment of the silicon carbide film with molecules of inert gas. Increasing the ratio of Si-C bonds in the film provides greater hardness and high elastic modulus in the silicon carbide film.

The following example illustrates a dual damascene structure in which a silicon carbide layer deposited according to the present invention can be used. FIG. 2a-2i shows a

dual damascene structure in which a silicon carbide layer deposited according to the present invention can be used. A copper (Cu) layer (31) is first covered with a first silicon carbide layer (32). Since the silicon carbide layer (32) according to this embodiment is oxygen free with low leakage current and low dielectric constant, it is suggested to be the most suitable material to use as a copper diffusion barrier layer. Before depositing the silicon carbide layer (32), the copper surface can be improved by removing any copper oxide that may be remaining on the surface. Typically a hydrogen (H₂) or an ammonia (NH₃) or methane (CH₄) plasma based reduction is used before the deposition of silicon carbide layer (32). This copper surface reduction to remove CMP residue can be performed in a PECVD chamber.

After the deposition of silicon carbide layer (32), a first inter level dielectric, in this case SiOC layer (33), is deposited. After the deposition of the SiOC layer (33), the second silicon carbide layer (34) and second inter level dielectric, in this case SiOC layer (35) and the silicon carbide layer (36), are deposited in sequence as shown in Fig.2a. A photo resist (37) is then coated on top of the third silicon carbide layer (36) as shown in Fig.2b. To form via holes and trenches, any suitable methods can be employed. The following is an example:

A via hole (39) is formed by etching. The process of forming a via hole is stated as follows: First a photo resist (37) is removed (38) as shown in Fig.2b. Next, a via etching is commenced through the third silicon carbide layer (36) to the first silicon carbide layer (32) as shown in Fig.2c. Finally, a portion of first silicon carbide layer (32) is etched to expose the metal line.

After via realization, trench patterning commences. First, a photo resist (37) is removed as shown in Fig.2d. Next, trench (41) is formed through etching third silicon carbide layer (36) to second silicon carbide layer (34) as shown in Fig.2e. The second silicon carbide layer (34) prevents the etching of the second SiOC layer (35) from continuing into the first SiOC layer (33).

A copper barrier layer such as TaN or TiN (42), is formed inside the via hole, which also covers top of the resist as shown in Fig.2f. A copper seed layer (43) is further deposited by PVD, or the like. Thereafter copper (44) is then deposited in the hole by electric plating or the like. By CMP or the like, the copper barrier layer (42), the copper (44), the resist (37) and the third silicon carbide layer (36), are removed so that the surface (45) is exposed.

A silicon carbide layer can also be deposited as a passivation layer (not shown) for protecting the device from scratching. The silicon carbide dielectric diffusion barrier (DDB) layer is important as it effectively prevents copper diffusion into the SiOC layers. This is due to the DDB layer having a low leakage current.

The leakage current and stress of conventional silicon carbide barrier layer at 1MV/cm is approximately 1×10^{-7} A/cm² and 100MPa when compared to that of approximately 1×10^{-9} A/cm² and above 200MPa respectively in a silicon carbide barrier layer fabricated as described herein. Thus, using a conventional silicon carbide barrier layer, as opposed to a silicon carbide layer fabricated as described herein, at an electric field of 2MV/cm, maintains the same effectiveness in preventing the copper diffusion. Furthermore, the resulting silicon carbide layer has a relatively low dielectric constant, typically around 4.5 and 5.0, depending on the mixture and ratio of low frequency to the total frequency generated during deposition, and also depending on the ratio of gases used to form the silicon carbide.

The film formation was conducted according the deposition conditions shown in Table 4 below.

TABLE 4

Parameter	Condition A	Condition B	Condition C
Tetra-methylsilane (TMS) flow rate (sccm)	180	200	180
Ammonia (NH ₃) flow rate (sccm)	250	250	250
Nitrogen (N ₂) flow rate (sccm)	600	600	600
Helium (He) flow rate (sccm)	2600	3000	2600
Pressure (Pa)	665	700	665
Low RF Power (W)	70	100	100
High RF Power (W)	550	550	550
Substrate Temperature (°C)	380	380	380

An as-deposited silicon carbide layer has a dielectric constant and leakage current at 1MV/cm less than about 5.0 and 1×10^{-8} A/cm², respectively, making it suitable for use as an

insulating material in integrated circuits. The details of the film properties such as dielectric constant, leakage current and film stress of the silicon carbide layer deposited according to the deposition conditions A, B and C is shown in Table5. The dielectric constant of the silicon carbide layer is tunable, in that it can be varied as a function of the ratio of the mixed frequency RF powers. In particular, as the ratio of the low frequency RF power to the total mixed powers decreases, the dielectric constant of the silicon carbide layer also decreases.

The dielectric constant of the silicon carbide layer can also be tuned as a function of the composition of the gas mixture during layer formation. As the carbon concentration in the gas mixture increases, the carbon content of the as-deposited silicon carbide layer increases, making the silicon carbide film less dense and dielectric constant decrease. Also, as the carbon concentration of the as deposited silicon carbide layer increases, the hydrophobic properties thereof increases making such layers suitable for use as moisture barriers in integrated circuits.

In addition, the as-deposited silicon carbide layer has no oxygen content. It is believed that such an oxygen free silicon carbide layer minimizes metal diffusion and improves the barrier layer properties. For example, the as-deposited silicon carbide layer has a current blocking ability at 1MV/cm that is less than that about $1 \times 10^{-8} \text{ A/cm}^2$, which is suitable for minimizing cross-talk between integrated circuit interconnect structures.

The etching performance of silicon carbide materials shows that the etch selectivity, based on RIE (reactive ion etching) etching mode, between SiOC and silicon carbide described herein was from 5 to 10.

TABLE 5

Film type	Film Stress Compressive (MPa)	Dielectric constant	Leakage current at 1MV/cm (A/cm ²)
SiCN (Condition A)	220 ± 20	4.6 ± 0.1	$<3 \times 10^{-9}$
SiCN (Condition B)	270 ± 20	4.7 ± 0.1	$<4 \times 10^{-9}$
SiCN (Condition C)	280 ± 20	4.8 ± 0.1	$<5 \times 10^{-9}$